Preparation of Paper, Cardboard and Pasteboard

Description

The invention relates to a process for the preparation of paper, cardboard and pasteboard by draining a pulp containing interferents in the presence of fixing agents based on hydrolyzed homopolymers and/or copolymers of N-vinyl formamide and retention agents.

EP-A 0,216,387 discloses that copolymers of from 95 to 10 mol% of N-vinyl formamide and from 5 to 90 mol% of an ethylenically unsaturated monomer selected from the group consisting of vinyl acetate, vinyl propionate, C_1-C_4 alkylvinyl ethers, N-vinylpyrrolidone, the esters, nitriles and amides of acrylic acid and methacrylic acid are added to the pulp in an at least partially hydrolyzed form, in which from 30 to100 mol% of the formyl groups are eliminated from the copolymers with the formation of amino groups, in amounts of from 0.1 to 5 wt%, based on dry fibers, prior to sheet formation, as wet and dry sealing agents for paper.

US-A 4,421,602 discloses that it is possible to use partially hydrolyzed homopolymers of N-vinyl formamide as retention agents, draining agents and flocculating agents for the preparation of paper.

Since the water circuits in paper mills become increasingly concentrated, there accumulate in the recycled water anionic compounds which strongly impair the activity of cationic polymeric processing chemicals during pulp drainage and also the retention of fillers and fibrous materials. In order to effect drainage of pulps containing interferents using cationic polymers it is therefore the usual practice to carry out the drainage of these pulps additionally in the presence of a fixing agent. Examples of the fixing agents used are condensates of dicyanodiamide and formaldehyde or condensates of dimethylamine and epichlorohydrin, cf Tapy Journal, August 1988, pp 131 to 134.

EP-A 0,438,707 discloses a process for the preparation of paper, cardboard and pasteboard by draining a pulp containing interferents in the presence of fixing agents and retention agents. The fixing agents used are hydrolyzed homopolymers and/or copolymers of N-vinylformamide having a degree of hydrolysis of at least 60%.

According to the teaching of EP-A 0,649,941 the deposition of interferents in a paper-making machine on, for example, metallic surfaces, screens and felts is reduced due to the fact that there is added to the pulp a water-soluble copolymer containing at least 5 mol% of an N-vinylcarboxamide or a hydrolysate thereof. The degree of hydrolysis of N-vinyl carboxamides such as N-vinyl formamide, is stated in the examples to be from 5 to 20 mol%.

It is an object of the present invention to provide an improved process for the preparation of paper, cardboard and pasteboard, where better fixation of the interferents and an improved retaining, flocculating and draining action is achieved as compared with the known process.

According to the invention, this object is achieved by means of a process for the preparation of paper, cardboard and pasteboard by draining a pulp containing interferents in the presence of fixing agents based on hydrolyzed homopolymers and/or copolymers of N-vinylformamide and retention agents, provided that the degree of hydrolysis of the N-vinyl formamide units incorporated as polymerized units is from 25 to 55 %.

In the process of the invention pulps are used for the preparation of which all fiber grades or mixtures of fibers are suitable. The preparation of the pulp is in practice usually carried out using water which is at least partially or even completely recycled by the paper-making machine. This water can be either clarified or unclarified backwater or a mixture of such waters. The recycled water contains more or less large amounts of so-called interferents which are known to greatly impair the activity of the cationic retention agents and draining agents or the "runnability" of the paper-making machine, cf H. L. Baumgarten, Das Papier, Vol. 38, Number 10-A, pp V121 to V125 (1984). These interferents exist in both soluble and insoluble, colloidal forms. Examples of such soluble interferents are humic acids, lignin sulfonate, silicic acids and wood extractives. Insoluble, lipophilic/hydrophobic interferents - so-called stickies or white-pitch - come for example from processing chemicals used in paper-making, from binding agents used for coating paper and pasteboard, from adhesives used in paper processing (these may be eg self-adhesives, dispersed adhesives or hot-melt adhesives), from printing ink binders or from materials used in paper processing. The concentration of such interferents in the pulp can be characterized using, for example, the sum parameter chemical oxygen demand (COD value). The COD values of the interferent-containing pulps are for example from 300 to 30,000 and are preferably from

1,000 to 20,000 mg of oxygen per kilogram of the aqueous phase of the pulp.

Suitable fibrous materials for the preparation of the pulps are all commonly used materials such as lignocellulose, bleached and unbleached cellulose and also pulps of all annual plants. Lignocellulose includes for example wood pulp, thermomechanical pulp (TMP), chemo-thermomechanical pulp (CTMP), pressure-ground pulp, semichemical pulp, high-yield cellulose and refiner mechanical pulp (RMP). The cellulose used may be for example sulfate, sulfite and soda pulps. Use is preferably made of unbleached cellulose, also termed unbleached kraft pulp. Suitable annual plants for the preparation of pulps are for example rice, wheat, sugarcane and hemp. In the preparation of the pulps use is also made of waste paper, which is used alone or mixed with other fibrous materials.

According to the invention, the fixing agents used for pulps containing interferents are hydrolyzed homopolymers and/or copolymers of N-vinylformamide having a degree of hydrolysis of from 25 to 55 %, together with retention agents.

Polymers of N-vinyl formamide in which the degree of hydrolysis of the N-vinyl formamide units incorporated as polymerized units is from 25 to 55 % have a surprisingly improved fixing action compared with the fixing agents disclosed in EP-A 0,438,707 and having a degree of hydrolysis of at least 60 % and the partially hydrolyzed polymers of N-vinyl carboxamides having a degree of hydrolysis of from 5 to 20 %, which are disclosed in EP-A 0,649,941. Such pronounced increase in the fixing action could not have been expected from the prior art.

Polymers of N-vinyl formamide having a degree of hydrolysis of from 25 to 55 % are known, cf the above references EP-A 0,216,387 and US-A 4,421,602. In order to prepare such polymers, N-vinyl formamide is first of all polymerized alone or, if desired, together with copolymizable ethylenically unsaturated monomers, and in a second reaction step the formyl group is eliminated from the N-vinyl formamide units incorporated as polymerized units with the formation of amino groups. Examples of suitable hydrolyzing agents are mineral acids such as hydrogen halides which can be used in the vapor phase or in aqueous solution. We prefer to use hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid and also organic acids such as C_1-C_5 carboxylic acids or aliphatic or aromatic sulfonic acids. For each formyl group equivalent to be eliminated from the polymers there are required for example from 0.05 to 2, preferably from 1 to 1.5, mole equivalents of an

acid. The hydrolysis can also be carried out with the assistance of bases, eg metal hydroxides, particularly alkali metal and alkaline earth metal hydroxides. Use is preferably made of sodium hydroxide or potassium hydroxide. The hydrolysis may also be carried out in the presence of ammonia or amines. To prepare polymers to be used in accordance with the present invention the hydrolysis is carried to a point at which the degree of hydrolysis of the total number of N-vinyl formamide units present in the polymer is from 25 to 55 %, preferably from 30 to 50 %.

Particularly suitable comonomers for the preparation of copolymers of N-vinyl formamide are vinyl formate, vinyl acetate, vinyl propionate, C_1-C_4 alkylvinyl ethers, N-vinylpyrrolidone, and esters, nitriles and amides of acrylic acid or methacrylic acid. The esters of acrylic acid and methacrylic acid are derived, for example, from alcohols containing from 1 to 6 carbon atoms. The copolymers preferably contain from 95 to 10 mol % of N-vinyl formamide and from 5 to 90 mol % of at least one ethylenically unsaturated monomer. We particularly prefer to use hydrolyzed polymers which can be prepared by polymerizing

(a) from 100 to 10 mol % of N-vinyl formamide and

(b) from 0 to 90 mol % of vinyl formate, vinyl acetate and/or vinyl propionate

and from which from 25 to 55 % of the vinyl formamide units incorporated as polymerized units are eliminated on termination of the polymerization, with the formation of vinyl amine units. When hydrolysis is carried out using acids, the corresponding ammonium salts are obtained, whilst hydrolysis using bases produces the corresponding amines. When copoylmers of N-vinyl formamide are hydrolzed with vinyl esters, the vinyl ester units present as polymerized units in the copolymer are partially or completely converted to vinyl alcohol units.

The homopolymers and copolymers of N-vinyl formamide having a degree of hydrolysis of from 25 to 55 % have K-values of for example from 30 to 150 and preferably from 60 to 90 (determined by the method proposed by H. Fikentscher on a 1 % strength solution in water at 25°C). The 25 to 55 % hydrolyzed N-vinyl formamide polymers to be used as fixing agents are used in the process of the invention in conventional amounts, ie amounts of from 0.02 to 2 and preferably from 0.05 to 0.5 wt% based on dry pulp.

The fixing agents are used in combination with retention agents. The retention agents used can be all polymeric materials that have been described as being suitable for this purpose. Thus the partially hydrolyzed homopolymers of N-vinyl formamide that are disclosed in US-A 4,421,602 can be used as retention agents. The degree of hydrolysis of the N-vinyl formamide units incorporated as polymerized units can be from 1 to 100 %. However unhydrolyzed polymers of N-vinyl formamide can be used as retention agents, if desired. Such polymers have for example K-values of at least 160 and preferably from 180 to 300 (determined by the method proposed by H. Fikentscher on a 5 % strength aqueous solution of common salt at 25oC and a polymer concentration of 0.5 wt%).

Further suitable retention agents are for example polyacrylamides, which can be used in an unmodified form or in a cationically or anionically modified form. Copolymers of acrylamide or methacrylamide are cationically modified for example by copolymerization with dialkylaminoethyl acrylates or dialkylaminoethyl methacrylates. Particularly interesting retention agents in this case are copolymers of acrylamide and N,N-dimethylaminoethyl acrylate or copolymers of acrylamide and N,N-diethylaminoethyl acrylate. The basic acrylates are present in the copolymers for example in amounts of from 5 to 70 and preferably from 8 to 40 mol% and preferably exist in an acid-neutralized or quaternized form. The quaternization can take place using, for example, methyl chloride or dimethyl sulfate.

Acrylamide and methacrylamide may also be anionically modified by copolymerization with monoethylenically unsaturated carboxylic acids. High molecular weight copolymers of for example acrylamide and acrylic acid are known retention agents. The concentration of anionic comonomers in the copolymers is for example from 5 to 50 and preferably from 10 to 40 wt%. The cationically or anionically modified poly(meth)acrylamides have for example K-values of at least 180 (determined by the method proposed by H. Fikentscher on a 5 % strength aqueous solution of common salt at 25oC and a polymer concentration of 0.5 wt%).

Examples of cationic retention agents are polyethyleneimines, polyamines having molar masses of more than 50,000, polyamidoamines, which are optionally cross-linked by grafting with ethyleneimine and subsequent cross linkage with for example polyethylene glycol dichlorohydrin ethers according to the teaching of DE-C 2,434,816 or using epichlorohydrin, polyetheramines, polyvinylimidazoles, polyvinylimidazolines, polyvinyltetrahydropyridines, polydialkylaminoalkylvinyl ethers, polydialkylaminoalkyl (meth)acrylates in a protonized or quaternized form, polydiallyl-

dialkylammonium halides such as, in particular polydiallyldimethyl-ammonium chloride. Particularly preferred retention agents are the polyamidoamines disclosed in the aforementioned DE-C 2,434,816, these having been grafted with ethyleneimine and subsequently cross-linked.

Other retention agents that can be used are the microparticle systems disclosed in the literature comprising high molecular weight polyacrylamides and bentonite, where a high molecular weight cationic polyacrylamide is first added to the pulp, which is then subjected to a shearing action before bentonite is added. Processes of this type are for example the subject matter of EP-A 0,235,893 and EP-A 0,335,575.

The preparation of paper, cardboard and pasteboard takes place in the process of the invention in the presence of N-vinyl formamide polymers, which are hydrolyzed to an extent of from 25 to 55 %, as fixing agent, and also in the presence of the retention agents usually employed in the paper-manufacturing industry, it being possible to use non-ionic, cationic or anionic retention agents for this purpose. However, we prefer to use cationic retention agents. The retention agents are usually employed in an amount of from 0.01 to 0.2 wt% based on dry pulp. The ratio of fixing agent used in the invention to retention agent is for example from 1:2 to 5:1. Preferably the 25 to 55 % hydrolyzed N-vinyl formamide polymer is first added to the pulp as fixing agent, followed by the retention agent. However, the fixing agent and retention agent can be simultaneously fed to the pulp, if desired.

The K-values of the polymers were determined by the method proposed by H. Fikentscher, Zellulose-Chemie, Vol. 13, 48 to 64 and 71 to 74 (1932) using a 1 % strength solution in water at a temperature of 25°C.

The fixing agents used were the following polymers:

Polymer 1:

Polyvinyl formamide, degree of hydrolysis 20 %, K-value 90 (Fikentscher; measured on a 1 % strength solution in water at a temperature of 25°C)). Fixing agent according to prior art as disclosed in EP-A 649,941.

Polymer 2:

Polyvinyl formamide, degree of hydrolysis 30 %, K-value 90 (Fikentscher; measured on a 1 % strength solution in water at a temperature of 25°C). The fixing agent used is that proposed in the invention.

Polymer 3:

Polyvinyl formamide, degree of hydrolysis 50 %, K-value 90 (Fikentscher; measured on a 1% strength solution in water at a temperature of 25°C).

Polymer 4:

Polyvinyl formamide, degree of hydrolysis 70 %, K-value 90 (Fikentscher; measured on a 1 % strength solution in water at a temperature of 25°C). Example of prior art as disclosed in EP-A 438,707.

The retention agent used is a commercially available polyamidoamine, which has been grafted with ethyleneimine and cross-linked with a bischlorohydrin ether of polyethylene glycol, cf Example 3 of DE-B 2,434,816.

Preparation of sheets of paper

To an aqueous pulp slurry of TMP (thermomechanical pulp) having a consistency of 2 % there was added, after making aliquots, the amount stated in Table 1 of an aqueous dispersion of coated brokes, as sticky interferent, to each aliquot. To each of the aliquot samples of this pulp there was added an equal amount of the aforementioned cationic retention agent. Following thorough mixing and filtering of the flocculated pulp the filtrate was examined by a laser-reading method to determine the number of particles. Such measurement took place by the method described in Nordic Pulp & Paper Research Journal, No. 1-1994 (9), 26-30 and 36 (1994). Of decisive significance as regards the activity of the system is the relative total volume of these stickies for a dosage of fixing agent of 0.05 %, because this amount is equivalent to the amounts used in the paper-making process.

Table 1

Fixing Agent	Fixing agent/retention agent, based on weight of pulp [%]	Relative total volume of stickies [%]
Polymer 1 (for comparison)		
a)	0	100
b)	0.01	59.5
c)	0.02	53.5
d)	0.05	40.3
e)	0.10	24.4
f)	0.20	17.2
Polymer 2 (invention) Example		
-	0	100
1	0.01	47.3
2	0.02	31.9
3	0.05	11.3
4	0.10	8.1
5	0.20	8.0
Polymer 3 (invention) Example		
-	0	100
6	0.01	54.5
7	0.02	44.3
8	0.05	35.1
9	0.10	24.1
10	0.20	17.0
Polymer 4 (for comparison)		
a)	0	100
b)	0.01	71.2
c)	0.02	52.3
d)	0.05	40.2
e)	0.10	30.8
f)	0.20	28.7

We claim:

1. A process for the preparation of paper, cardboard and pasteboard by draining a pulp containing interferents in the presence of fixing agents based on hydrolyzed homopolymers and/or copolymers of N-vinyl formamide and retention agents, wherein the degree of hydrolysis of the N-vinyl formamide units incorporated as polymerized units is from 25 to 55 %.

2. A process as defined in claim 1, wherein use is made of hydrolyzed homopolymers of N-vinyl formamide having a degree of hydrolysis of from 30 to 50 % and a K-value of from 30 to 150 (determined by the method proposed by H. Fikentscher on a 1% strength solution in water at 25°C).

3. A process as defined in claim 2, wherein the retention agent used is a cationicpolymer.

4. A process as defined in claim 1 or claim 2, wherein the retention agent used is an anionic retention agent.

5. A process as defined in any of claims 1 to 4, wherein the fixing agent and retention agent are used in a ratio, by weight, of from 1:2 to 5:1.

6. A method of using a hydrolyzed homopolymer and/or copolymer of N-vinyl formamide in which the degree of hydrolysis of the N-vinyl formamide units incorporated as polymerized units is from 25 to 55 %, as fixing agent, in combination with a cationic or anionic retention agent for the preparation of paper, cardboard and pasteboard by draining a pulp containing interferents.

Process for the Preparation of Paper, Cardboard and Pasteboard

Abstract of the disclosure:

A process for the preparation of paper, cardboard and pasteboard by draining a pulp containing interferents in the presence of fixing agents of homopolymers and/or copolymers of N-vinyl formamide having a degree of hydrolysis of the N-vinyl formamide units incorporated as polymerized units of from 25 to 55 %, and retention agents.